SYNTHESIS OF TRIMETHYLAMINOPYRROLYLOBORANE

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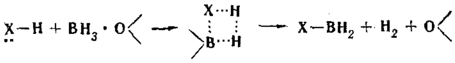
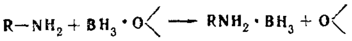
Pyrrolyloborane, fixed as a complex with trimethylamine, was obtained by the reaction of equimolar amounts of BH_3·tetrahydrofuran and pyrrole in tetrahydrofuran. It was thereby demonstrated that prior coordination of borane with the free electron pair of the nitrogen atom that is not included in the aromatic π system is not compulsory for the reaction of borane–ether complexes with five-membered heterocyclic aromatic amines.

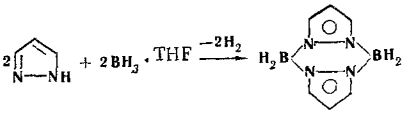
It is known that borane–ether complexes react readily with compounds of the XH type (X = O, halogen, S) with hydrogen evolution [1,2]. In all cases, the reaction proceeds through a four-membered transition state in which the boron atom is coordinated via the free electron pair with the X atom bonded to the labile hydrogen.



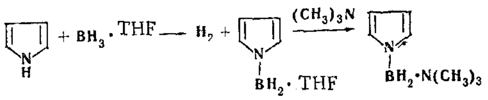
At the same time, the reaction of aliphatic amines with BH_3–ether complexes at ambient temperature proceeds via a different scheme [3].



However, borane–ether complexes [with tetrahydrofuran (THF), for example] react with pyrazoles under mild conditions with hydrogen evolution to give the so-called pyrazaboles [4].



It has been thought that here also the first step of the reaction is prior coordination of borane with the free electron pair of the nitrogen atom that is not included in the aromatic π system [4]. To verify this hypothesis, we have introduced pyrrole, in which this sort of prior coordination is impossible, into the reaction. Pyrrole reacts smoothly at room temperature with an equimolar amount of BH_3·THF in THF with the evolution of 1 mole of hydrogen. The pyrrolyloborane obtained was fixed as a crystalline complex with trimethylamine.*



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*The preparation of a complex of pyrrolyloborane with triethylamine at high temperature from pyrrole and a borane–triethylamine complex was reported in [5].

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Treatment of a solution of pyrrolyloborane in THF with liquid ammonia gave a complex ( N–$BH_2 \cdot NH_3$), which was an oil that decomposed rapidly on storage in air and by the action of protic solvents.

Thus we have demonstrated that the coordination of borane with the free electron pair of the nitrogen atom that is not included in the aromatic π system is not a necessary condition for the reaction (similar to the formation of "pyrazaboles") of five-membered aromatic heterocyclic amines.

EXPERIMENTAL

Trimethylaminopyrrolyloborane. A 0.5 g (7.5 mmole) sample of freshly distilled pyrrole was added with stirring at 20 deg C to 0.1 g (7.5 mmole) of BH_3 (4.75 ml of a 1.58 N solution in THF) (160 ml of H_2 was evolved after 15 min), the mixture was cooled to −30 deg, and 3 ml of trimethylamine was added. The solvent was removed by vacuum distillation, and the residue was extracted with ether. Evaporation of the ether yielded 0.69 g (69%) of trimethylaminopyrrolyloborane with mp 63-65 deg that sublimed at 80 deg (1 mm). Found: C 60.91, 60.50; H 11.33, 11.05; B 7.84, 8.25; N 20.42, 20.62%. $C_7H_{15}N_2B$. Calculated: C 60.87; H 10.87; B 7.97; N 20.29%. IR spectrum (cm^{-1}): 680, 700 weak, 745 very strong, 840 strong, 1080-1090 weak doublet, 1080 strong, 1100, 1165 very strong, 1190, 1235, 1250-1260 doublet, 1480, 2300 triplet, 2400 strong triplet, 2940 weak, 3000 weak, 3060 weak.

The B" NMR spectrum in CCl_4 was recorded with an RS-56 spectrometer with an operating frequency of 19.27 MHz with $BF_3 \cdot Et_2O$ as the standard: +0.8 ppm, J 90 ±10 Hz. The PMR spectrum in CCl_4 was recorded with a Varian DA-60 spectrometer using boron-proton double resonance: NCH_3 2.18 ppm (singlet), BH_2 2.47 ppm (singlet), aromatic ring protons 5.90 ppm (multiplet and 6.49 ppm (multiplet) (intensity ratio 1:1). The standard was hexamethyldisiloxane.

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